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(54) Title: CEMENT FORMULATION

(57) Abstract

This invention relates to a formulation for preparing a dry formulation for preparing an autoclave cured cementitious product comprising: a cementitious material; a siliceous material; and a dehydroxylated clay mineral.

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TITLE: **CEMENT FORMULATION**

FIELD OF THE INVENTION

This invention relates to a formulation for preparing an autoclave cured cementitious material, to a method of preparing a cementitious product using the formulation and to a shaped article capable of being prepared therefrom.

BACKGROUND OF THE INVENTION

Autoclave cured cementitious materials are commonly used both with and without reinforcement fibres to manufacture many building products. Un-reinforced autoclave aerated concrete (AAC) building blocks and cellulose fibre reinforced concrete (FRC) flat or profiled sheets and FRC pipes are examples of such products.

The raw materials used for the manufacture of autoclave cured cementitious products are typically reinforcing fibre (if required), ground sand, cement and/or lime, water and minor additives. However, it has been difficult to date to obtain unpressed autoclave cured cementitious products that are as impermeable to water as post-pressed equivalents. Post-pressing occurs after formation of the product.

OBJECT OF THE INVENTION

It would be desirable to obtain an autoclave cementitious product that has low water permeability.

DISCLOSURE OF THE INVENTION

According to a first aspect of the invention there is provided a dry formulation for preparing an autoclave cured cementitious product comprising:

a cementitious material;

a siliceous material; and

a dehydroxylated clay mineral.

According to a second aspect of the invention there is provided an aqueous formulation for preparing an autoclave cured cementitious product comprising:

a cementitious material;

a siliceous material,

a dehydroxylated clay mineral; and

water.

Throughout this specification, unless indicated otherwise where there is reference to wt%, all values are with respect to the formulation on a dry materials weight basis prior to addition of water and processing.

The siliceous material is preferably present in an amount of from 10-80wt%, more preferably 30-70wt%, most preferably 40-65wt%. Preferably the siliceous material is ground sand (also known as silica) or fine quartz. Preferably the siliceous material has an average particle size of 1-50 microns, more preferably 20-30 microns.

The cementitious material is preferably present in an amount of from 10-80wt%, more preferably 30-70wt%, most preferably 35-50wt%. Preferably the cementitious material is cement and/or lime and/or lime containing material and includes Portland cement, hydrated lime, lime or mixtures thereof. Preferably the cementitious material has an average particle size of 1-50 microns, more preferably 20-30 microns.

The dehydroxylated clay mineral can be dehydroxylated kaolin (also known as metakaolin), dehydroxylated bentonite, dehydroxylated montmorillonite, dehydroxylated illite, dehydroxylated muscovite or dehydroxylated phlogopite etc. Preferably the dehydroxylated clay mineral is metakaolin. Metakaolin (Al_2O_3 .$2SiO_2$) is a reactive aluminium silicate pozzolan formed by thermal activation (dehydroxylation) of kaolin in the temperature range 450-800°C. The dehydroxylated clay mineral is preferably present in an amount of from 0.25-30wt%, more preferably 1-25wt%, most preferably 2-

12wt%. Preferably the dehydroxylated clay mineral has an average particle size of 1-50 microns, more preferably 4-8 microns. The dehydroxylated clay mineral may be in a pure or impure form and includes, impure natural clays containing dehydroxylated clay minerals together with other components. Suitable natural clays include tropical soils, and laterite soils. Also suitable are processed natural clays such as black colliery spoil and slate waste.

The formulations can include a fibrous material capable of producing a fibre reinforced product. Suitable fibrous materials include cellulose such as softwood and hardwood cellulose fibres, non wood cellulose fibres, asbestos, mineral wool, steel fibre, synthetic polymers such as polyamides, polyesters, polypropylene, polyacrylonitrile, polyacrylamide, viscose, nylon, PVC, PVA, rayon, glass, ceramic or carbon. Cellulose fibres produced by the Kraft process are preferred. Preferably the fibrous materials are present in a concentration of 0-25wt%, more preferably 2-16wt%, most preferably 5-12wt%. When cellulose fibres are used, they are preferably refined to a degree of freeness of between 0 and 800 Canadian Standard Freeness (CSF), more preferably 200-500 CSF.

The formulations can contain 0-40wt% of other additives such as fillers such as mineral oxides, hydroxides and clays, metal oxides and hydroxides, fire retardants such as magnesite, thickeners, silica fume or amorphous silica, colorants, pigments, water sealing agents, water reducing agents, setting rate modifiers, hardeners, filtering aids, plasticisers, dispersants, foaming agents or flocculating agents, water-proofing agents, density modifiers or other processing aids.

According to a third aspect of the invention there is provided a method for forming an autoclave cured cementitious product comprising:

adding a cementitious material, a siliceous material, a dehydroxylated clay mineral and optionally other additives to water to form a slurry;

forming a green shaped article by dewatering the slurry;

optionally pressing the article; and

curing the article in an autoclave.

Green shaped articles may be formed from the water borne slurry by any of a number of conventional processes such as the Hatschek sheet process, the Mazza pipe

process, the Magnani sheet process, injection moulding, extrusion, hand lay-up, moulding, casting, filter pressing, flow on machine, roll forming, etc., with or without post-formation pressing. After forming, the green article is preferably precured for a short time, preferably 0 to 30 hours then cured by autoclaving preferably in a steam pressurised vessel preferably at 120 to 200°C for 3 to 30 hours, most preferably less than 24 hours. The length of time and temperature chosen for curing is dependant on the formulation, the manufacturing process and the form of the article.

According to a fourth aspect of the invention there is provided a cementitious product comprising the autoclave cured reaction product of a dehydroxylated clay mineral, a cementitious material, a siliceous material and optionally other additives.

According to a fifth aspect of the invention there is provided a cementitious product comprising the autoclave cured reaction product of a fibrous material, a dehydroxylated clay mineral, a cementitious material, a siliceous material and optionally other additives.

Preparing autoclave cured products by adding a dehydroxylated clay mineral to the formulation can improve the strength and toughness of the product and reduce water permeability and hygroscopic moisture movement.

PREFERRED EMBODIMENT OF THE INVENTION

The invention will now be described by way of preferred embodiments with reference to the following examples.

Throughout Examples 2 to 6 and 8 water permeability is determined by gluing a 1.2m tall tube to the surface of a test specimen, filling water into the tube to a predetermined height and determining its time rate of fall compared to a control.

Carbonated moisture movements are determined after the articles (i.e. filter pads) have been subjected to carbon dioxide gas.

Flexural toughness is the total energy per unit volume absorbed by test specimens up to the point of maximum load.

EXAMPLE 1

Use of metakaolin in a non-reinforced cement/silica matrix.

A bench scale experiment was performed. Standard un-reinforced cement/silica test cubes, bars and disks based on off-white cement, were prepared according to a

conventional procedure (formulation 1) without post-pressing and used as a control. Two formulations in accordance with the invention were also prepared without post-pressing (formulations 2 and 3). In formulations 2 and 3 metakaolin was incorporated into the matrix as a replacement for some of the silica. Compositions and amounts of each formulation are shown in Table 1a. The cement was an off-white cement of greater reactivity than ordinary grey general purpose cement. Specimens were all autoclave cured for eight hours at 180°C.

Table 1a

Formulation	Off-white Cement	Silica	Metakaolin
1	40.0wt%	60.0wt%	0.0wt%
2	40.0wt%	58.5wt%	1.5wt%
3	40.0wt%	57.0wt%	3.0wt%

Table 1b

Formulation	1	2	3
Level of metakaolin addition, wt%	0	1.5	3.0
Cube compressive strength, MPa	110	99	91
Bar un-carbonated moisture movement, %	0.25	0.21	0.21
Disk drying mass loss, % per hour	6.2	5.3	4.8

The average measured physical properties and drying rates are shown in Table 1b. Drying rate was determined by saturating disks under water until they reached constant mass, drying them in a forced draft oven at 55°C for one hour and determining the mass (of water) lost by drying.

It can be seen from Table 1b that matrices formulated according to the invention (formulations 2 and 3) exhibit lower drying rates, i.e. high resistance to water permeation. Further the un-carbonated moisture movements of the inventive formulations are reduced. All of the observed compressive strengths are well above the 85MPa considered reasonable for actual product performance.

EXAMPLE 2

Use of metakaolin in cellulose fibre-reinforced concrete filter pads.

A bench scale experiment was conducted. Filter pads of cellulose fibre-reinforced concrete with a 40:60 (weight basis) cement:silica ratio were prepared without post-pressing according to a conventional procedure. Formulation 4 was used as a control. Two formulations in accordance with the invention were then prepared with metakaolin incorporated into the matrix (formulations 5 and 6). The composition and amounts of each formulation are shown in Table 2a. Specimens were all autoclave cured for eight hours at 180°C.

Table 2a

Formulation	Cellulose	Cement	Silica	Metakaolin	Fire Retardant
4	8.0wt%	35.2wt%	52.8wt%	0wt%	4.0wt%
5	8.0wt%	36.8wt%	53.2wt%	2.0wt%	0wt%
6	8.0wt%	36.8wt%	51.2wt%	4.0wt%	0wt%

Table 2b

Formulation	4	5	6
Cellulose freeness, CSF	450	450	450
Level of metakaolin addition, wt%	0	2.0	4.0
Saturated flexural strength, MPa	11.8	11.9	12.6
Saturated Young's modulus, GPa	2.9	2.6	3.4
Saturated flexural toughness, KJ/m3	11.0	11. 5	11.4
Uncarbonated moisture movement %	0.17	0.19	0.19
Carbonated moisture movement, %	0.43	0.45	0.47
Water permeation rate, ml/hr	1.00	0.50	0.38
Oven dry density, kg/m3	1270	1270	1270

The resulting average measured physical properties and water permeability rates (using a 1m high water column) are shown in Table 2b. Filter pads formulated

according to the invention (formulations 5 and 6) exhibit improved water permeation resistance without adverse effects on other physical properties.

EXAMPLE 3

Effect of cellulose freeness on water permeability reduction effect.

A bench scale experiment was conducted. Formulations were used containing cellulose having two different pulp freeness levels to make filter pads without post-pressing via a conventional procedure. Formulations 7 and 9 were used as a control. Formulations 8 and 10 were made in accordance with the present invention and contained 2wt% of metakaolin. Compositions and amounts of each formulation are shown in Table 3a. Specimens were all autoclave cured for eight hours at 180°C.

Table 3a

Formulation	Cellulose	Cement	Silica	Metakaolin	Fire Retardant
7	8.0wt%	35.2wt%	52.8wt%	0wt%	4.0wt%
8	8.0wt%	36.8wt%	53.2wt%	2.0wt%	0wt%
9	8.0wt%	35.2wt%	52.8wt%	0wt%	4.0wt%
10	8.0wt%	36.8wt%	53.2wt%	2.0wt%	0wt%

Table 3b

Formulation	7	8	9	10
Cellulose freeness, CSF	450	450	141	141
Level of metakaolin addition, wt%	0	2.0	0	2.0
Saturated flexural strength, MPa	11.8	11.9	10.5	11.3
Saturated Young's modulus, GPa	2.9	2.6	3.5	4.3
Saturated flexural toughness, KJ/m3	11.0	11.5	5.1	4.9
Uncarbonated moisture movement %	0.17	0.19	0.18	0.22
Carbonated moisture movement, %	0.43	0.45	0.42	0.36
Water permeation rate, ml/hr	1.00	0.50	0.71	0.47
Oven dry density, kg/m3	1270	1270	1270	1250

The physical properties and water permeation rates are shown in Table 3b. Comparison of the results for formulations 7, 8, 9 and 10 show that filter pads formulated according to the invention (formulations 8 and 10) exhibit improved water permeation resistance for both pulp freeness levels investigated.

EXAMPLE 4

Effect of method of metakaolin addition on permeability.

A bench scale experiment was conducted. Filter pads were prepared without post-pressing according to a conventional procedure. Formulations 11 and 13 were used as controls. Formulations 12 and 14 in accordance with the invention contained metakaolin at a level of 2.0wt% using two different addition methods, namely (i) by addition to the matrix mix (formulation 12) and (ii) by addition to the cellulose fibre prior to batching of solids (formulation 14) so that the fibres were effectively pre-coated with the metakaolin. Compositions and amount for each formulation are shown in Table 4a. Specimens were all autoclave cured for eight hours at 180°C.

Table 4a

Formulation	Cellulose	Cement	Silica	Metakaolin	Fire Retardant
11	8.0wt%	35.2wt%	52.8wt%	0wt%	4.0wt%
12	8.0wt%	36.8wt%	53.2wt%	2.0wt%	0wt%
13	8.0wt%	35.2wt%	52.8wt%	0wt%	4.0wt%
14	8.0wt%	36.8wt%	53.2wt%	2.0wt%	0wt%

Table 4b

Formulation	11	12	13	14
Cellulose freeness, CSF	450	450	390	390
Level of metakaolin addition, wt%	-	2	-	2
Method of metakaolin addition	-	Mix addition	-	Fibre coated
Saturated flexural strength, MPa	11.8	11.9	11.1	12.5
Saturated Young's modulus, GPa	2.9	2.6	3.6	3.9
Saturated flexural toughness, KJ/m3	11.0	11.5	6.3	6.6
Uncarbonated moisture movement %	0.17	0.19	0.15	0.19
Carbonated moisture movement, %	0.43	0.45	0.43	0.43
Water permeation rate, ml/hr	1.00	0.50	1.00	0.43
Oven dry density, kg/m3	1270	1270	1330	1270

The physical properties and permeability rates are given in Table 4b, which shows filter pads formulated according to the invention (formulations 12 and 14) exhibit improved water permeation resistance for both methods of metakaolin addition.

EXAMPLE 5

Effect of metakaolin addition on toughness and moisture movements

A bench experiment was conducted. Filter pads were prepared without post-pressing using a conventional procedure. Formulation 15 was used as a control. Formulations 16 and 17 were prepared in accordance with the invention by incorporating metakaolin into the matrix by replacement of silica whilst maintaining the amount of cement. The silica:cement weight ratio for the control was 50:50. Compositions and amounts of each of the formulations are shown in Table 5a. Specimens were all autoclave cured for eight hours at 180°C.

Table 5a

Formulation	Cellulose	Cement	Silica	Metakaolin
15	8.0wt%	46.0wt%	46.0wt%	0wt%
16	8.0wt%	46.0wt%	44.0wt%	2.0wt%
17	8.0wt%	46.0wt%	36.0wt%	10.0wt%

Table 5b

Formulation	15	16	17
Cellulose freeness, CSF	465	357	465
Level of metakaolin addition, wt%	0%	2.0%	10.0%
Saturated flexural strength, MPa	14.6	13.8	12.2
Saturated Young's modulus, GPa	3.4	3.5	3.1
Saturated flexural toughness, KJ/m3	8.8	7.8	11.7
Uncarbonated moisture movement %	0.20	0.20	0.18
Carbonated moisture movement, %	0.52	0.49	0.46
Water permeation rate, ml/hr	0.51	0.41	0.23
Oven dry density, kg/m3	1300	1320	1290

The physical properties and resistance to permeation values are shown in Table 5b. Comparison of the results of formulations 15, 16 and 17 show that filter pads formulated according to the invention (formulations 16 and 17) exhibit improved water permeation resistance. At a 10wt% level of metakaolin addition (formulation 17) the saturated flexural toughness is significantly improved and post- and pre-carbonation moisture movement is reduced.

EXAMPLE 6

Effect of metakaolin and lime additions on toughness and moisture movement.

A bench experiment was conducted. Filter pads were prepared via a conventional procedure without post-pressing. Formulation 18 was used as a control. Formulations 19 and 20 were prepared in accordance with the present invention with metakaolin and hydrated lime in the relative weight proportions of 1:2 were incorporated into the matrix. In both the control and inventive formulations, a cement:silica ratio of 50:50 was maintained. Compositions and amounts for each formulation are given in Table 6a. Specimens were all autoclave cured for eight hours at 180°C.

Table 6a

Formulation	Cellulose	Cement	Silica	Metakaolin	Lime
18	8.0wt%	46.0wt%	46.0wt%	0wt%	0wt%
19	8.0wt%	38.5wt%	38.5wt%	5.0wt%	10.0wt%
20	8.0wt%	34.8wt%	34.8wt%	7.5wt%	15.0wt%

Table 6b

Formulation	18	19	20
Cellulose freeness, CSF	266	266	266
Level of metakaolin addition, wt%	0	5.0	7.5
Saturated flexural strength, MPa	13.5	11.6	9.6
Saturated Young's modulus, GPa	4.25	3.0	2.5
Saturated flexural toughness, KJ/m3	5.2	9.6	9.2
Uncarbonated moisture movement %	0.21	0.18	0.15
Carbonated moisture movement, %	0.45	0.42	0.40
Water permeation rate, ml/hr	0.21	0.21	0.30
Oven dry density, kg/cm3	1310	1270	1240

The physical properties and resistance to permeation values are shown in Table 6b. It is evident from the table that filter pads formulated according to the invention (formulations 19 and 20) exhibit reduced post- and pre-carbonation moisture movement. Further the flexural toughness is also improved. This is associated with a visible decrease in the oven dry density and a less than expected decrease in flexural strength and Young's modulus.

EXAMPLE 7

Effect of metakaolin addition on low density composites

A bench scale experiment was conducted. Filter pads all incorporating a density lowering, autoclave stable modifier additive were prepared via a conventional procedure without post-pressing. Formulations 21 and 23 were used as a control. Formulations 22 and 24 were prepared in accordance with the invention with metakaolin incorporated into the matrix by replacement of silica and cement while maintaining the cement:silica

ratio. Compositions and amounts of each of the formulations is shown in Table 7a. Specimens were all autoclave cured for eight hours at 180°C.

Table 7a

Formulation	Cellulose	Cement	Silica	Metakaolin	Additive
21	11.3wt%	31.5wt%	47.3wt%	0wt%	10.0wt%
22	11.3wt%	30. 4wt%	45.7wt%	2.7wt%	10.0wt%
23	11.3wt%	27.5wt%	41.3wt%	0wt%	20.0wt%
24	11.3wt%	25.3wt%	38.0wt%	5.4wt%	20.0wt%

Table 7b

Formulation	21	22	23	24
Cellulose freeness, CSF	380	380	380	380
Level of metakaolin addition, wt%	0	2.7	0	5.4
Saturated flexural strength, MPa	6.7	6.1	4.8	5.7
Saturated flexural toughness, KJ/m3	10.5	12.6	9.6	10.2
Uncarbonated moisture movement %	0.25	0.19	0.26	0.23
Carbonated moisture movement, %	0.40	0.44	0.45	0.64
Carbonation shrinkage, %	0.20	0.15	0.14	0.12
Permeability factor	241	138	138	47
Density, kg/m3	884	1016	913	923

The physical properties and permeability factor values are shown in Table 7b. The permeability factor is a proportionate measure of the rate at which water under pressure may be forced through a specimen in a permeability testing cell. Lower values indicate lower water permeability. It is evident from the table that filter pads formulated according to the invention (formulations 22 and 24) exhibit reduced un-carbonated moisture movement, reduced carbonation shrinkage values and reduced permeability to water . Further with metakaolin addition, the flexural toughness is improved (formulation 22) and the flexural strength is increased (formulation 24).

EXAMPLE 8

Use of Metakaolin as replacement to cement in cellulose fibre-reinforced cementitious composites

A full scale experiment was conducted. Cellulose fibre-reinforced cementitious sheets (6 mm thick) were made using the Hatschek process. Formulation 25 was used as control. Two formulations in accordance with the invention were then prepared with metakaolin incorporated in the matrix by partial replacement of cement (Formulations 26 and 27). The composition and amounts of each formulation are shown in Table 8a. All sheets were autoclave cured for eight hours at 180°C.

Table 8a

Formulation	Cellulose	Cement	Silica	Metakaolin	Pigment	Fire Retardant
25	8.0 wt%	35 wt%	60 wt%	0.0 wt%	4.0 wt%	4.0 wt%
26	7.0 wt%	29 wt%	54 wt%	6.0 wt%	4.0 wt%	0.0 wt%
27	7.0 wt%	25 wt%	58 wt%	6.0 wt%	4.0 wt%	0.0 wt%

Table 8b

Formulation	25	26	27
Cellulose Freeness, CSF	450	450	450
Level of metakaolin addition, wt%	0.0	6.0	6.0
Saturated flexural strength, MPa	12.47	12.30	12.40
Saturated flexural toughness, KJ/m3	12.50	10.50	9.50
Uncarbonated moisture movement, %	0.17	0.15	0.15
Water Permeation Rate, ml/hr	1.13	0.67	0.54
Saturated Young's modulus, GPa	4.54	5.07	5.15
Oven dry density, kg/m3	1400	1440	1400

Comparison of the results for formulations 25, 26 and 27 is shown in Table 8b. It can be seen that cellulose fibre-reinforced sheets formulated according to the invention

with metakaolin incorporated as cement replacement (formulations 26 and 27), exhibited comparable saturated flexural strengths and significantly less water permeation rates compared to sheets made with Formulation 25. It is further observed that uncarbonated moisture movements were reduced. The results achieved in this example show that, at the above indicated addition level, metakaolin contributes to the strength of cement deficient composites in addition to reducing their permeability rate and moisture movement.

The values for water permeability reduction evidenced by the un-pressed products using formulations in accordance with the invention as evidenced by the examples are values which would normally only be obtained by an additional step of post-pressing products with the attendant increase in density. It is believed that post-pressing will further enhance the observed reduction in water permeability.

Further from the examples it can be seen that metakaolin addition results in reduced un-carbonated and post-carbonation moisture movements of autoclave composites and in some cases to reduced carbonation shrinkage. Flexural toughness (the energy required to fracture a flexural test specimen) of the autoclave composites is also improved when metakaolin is present as an additive in the matrix forming material.

The formulations of the present invention are suitable for the production of autoclave cured cementitious products for both internal and external applications.

Although the invention has been described with reference only to selected examples, it will be appreciated by those skilled in the art that the invention may be embodied in many other forms.

CLAIMS

1. A dry formulation for preparing an autoclave cured cementitious product comprising:

a cementitious material;

a siliceous material; and

a dehydroxylated clay mineral.

2. A formulation according to claim 1 wherein the siliceous material is present in an amount of from 10 to 80 wt. % based on the total weight of the dry formulation.

3. A formulation according to claim 1 or 2 wherein the siliceous material is ground sand or fine quartz.

4. A formulation according to any one of claims 1 to 3 wherein the siliceous material has an average particle size of 1 to 50 microns.

5. A formulation according to any one of claims 1 to 4 wherein the cementitious material is present in an amount of from 10 to 80 wt. % based on the total weight of the dry formulation.

6. A formulation according to any one of claims 1 to 5 wherein the cementitious material is cement and/or lime and/or lime containing material.

7. A formulation according to any one of claims 1 to 6 wherein the cementitious material has an average particle size of from 1 to 50 microns.

8. A formulation according to any one of claims 1 to 7 wherein the dehydroxylated clay mineral is dehydroxylated kaolin, dehydroxylated bentonite, dehydroxylated montmorrilonite, dehydroxylated muscovite or dehydroxylated phlogopite.

9. A formulation according to claim 8 wherein the dehydroxylated clay mineral is dehydroxylated kaolin.

10. A formulation according to any one of claims 1 to 9 wherein the dehydroxylated clay mineral is present in an amount from 0.25 to 30 wt. % based on the total weight of the dry formulation.

11. A formulation according to any one of claims 1 to 10 wherein the dehydroxylated clay mineral has an average particle size of 1 to 50 microns.

12. A formulation according to any one of claims 1 to 11 further comprising a fibrous material.

13. A formulation according to claim 12 wherein the fibrous material is selected from cellulose, asbestos, mineral wool, steel fibre, synthetic polymers, glass, ceramic or carbon.

14. A formulation according to claim 13 wherein the fibrous material is cellulose having a degree of freeness of between 0 and 800 CSF.

15. A formulation according to any one of claims 12 to14 wherein the fibrous material is present in an amount up to 25 wt. % based on the total weight of the dry formulation.

16. A formulation according to any one of claims 1 to 15 further comprising at least one other additive selected from mineral oxides, mineral hydroxides, mineral clays, metal oxides, metal hydroxides, fire retardants, thickeners, silica fume, amorphous silica, colorants, pigments, water sealing agents, water reducing agents, setting rate modifiers, hardeners, filtering aids, plasticizers, dispersants, foaming agents, flocculating agents, water-proofing agents, density modifiers or other processing aids.

17. An aqueous formulation for preparing an autoclave cured cementitious product comprising:

a cementitious material;

a siliceous material;

a dehydroxylated clay mineral;

water; and optionally other additives.

18. A method for forming an autoclave cured cementitious product comprising:

adding a cementitious material, a siliceous material, a dehydroxylated clay mineral and optionally other additives to water to form a slurry;

forming a green shaped article by dewatering the slurry;

optionally pressing the article; and

curing the article in an autoclave.

19. A method according to claim 18, further comprising a fibrous material.

20. A method according to claim 18 or 19 wherein the green shaped articles are formed from the slurry with or without post-formation pressing, by means of one or more of the processes selected from the Hatshek sheet process, the Mazza pipe process, the Magnani sheet process, injection moulding, extrusion, hand lay-up, moulding, casting, filter pressing, flow on machine or roll forming.

21. A method according to any one of claims 18 to 20 wherein the green article is precured prior to curing.

22. A method according to any one of claims 18 to 21 wherein the article is cured by autoclaving in a steam pressurised vessel at 120 to 200°C for 3 to 30 hours.

23. A cementitious product comprising the autoclave cured reaction product of a dehydroxylated clay mineral, a cementitious material, a siliceous material and optionally other additives.

24. A cementitious product comprising the autoclave cured reaction product of a fibrous material, a dehydroxylated clay mineral, a cementitious material, a siliceous material and optionally other additives.

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/AU 96/00522

A. CLASSIFICATION OF SUBJECT MATTER

Int Cl[6]: C04B 14/10, 20/04, 28/02, 22/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC : C04B 14/10, 20/04, 28/02, 22/08, 31/20, 31/40, 13/00, 7/355

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
AU : IPC as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
DERWENT, CAS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 4104919 A (VEIT DENNERT KG) 20 August 1992 see whole document	1-13, 23-24
X	Derwent Abstract Accession No. 85-091806/15 Class LO2 SU 1114646 A (MARIISK POLY) 23 September 1984	17-20, 22-24
X	Derwent Abstract Accession No. 27516B/14 Class L02 SU 607813 A (BUILDING MAT CONS) 25 April 1978	1-13, 23-24

[X] Further documents are listed in the continuation of Box C

[X] See patent family annex

* Special categories of cited documents:

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"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search	Date of mailing of the international search report
28 October 1996	14.11.1996

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INTERNATIONAL SEARCH REPORT

International Application No.
PCT/AU 96/00522

C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	AU 40398/93 (HUELS TROISDORF AG) 28 October 1993 see whole document	17-18, 20-23
X	Derwent Abstract Accession No. 92327B/15 Class LO2 SU 655678 A (BELGOROD CON MAT) 8 April 1979	1-13, 17, 23-24
X	FR 2248246 A (COMMISSARIAT A L'ENERGIE ATOMIQUE) 16 May 1975 see whole document	17, 23-24

INTERNATIONAL SEARCH REPORT
Information on patent family members

International Application No.
PCT/AU 96/00522

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
DE	4104919						
SU	1114646						
SU	607813						
AU	40398/93	WO DE	9321126 4212229	DE JP	4236855 7506326	DE	4391555
SU	655678						
FR	2248246						

END OF ANNEX

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